INVESTIGATION OF QUINONES

XXVII.* REACTION OF 2-ARYLANTHRAQUINONETRIAZOLES WITH AMINES

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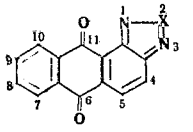
The action of primary and secondary amines on 2-arylanthraquinonetriazoles results in substitution of the hydrogen atom in the 4 position to form 4-amino derivatives. The activity of 2-arylanthraquinonetriazoles in amination is less than that of the previously studied anthraquinone-1,2,5-X-diazoles (X=O, S, Se). This is explained by the electron-donor effect of the aryl group in the 2 position and the lower degree of alternation of the bonds in the ring adjacent to the heteroring, which leads to a decrease in the effectiveness of transmission of the electron-acceptor effect to the reaction center in the 4 position.

In previous communications [2-5], it was demonstrated that, under the influence of a condensed heteroring, anthraquinonediazoles I-III display an unusual (for the 9,10-anthraquinone series) tendency for nucleophilic addition reactions. Similar reactivity might have been expected for 2-arylanthraquinonetriazoles IV, which are structurally similar to quinones I-III.



I X = O;
II X = S;
III X = Se;
IV X = NAr

2-Arylanthra[1,2-d]triazole-6,11-diones (IV) have been patented as vat dyes [6,7], but their chemical properties have not received special study. Quinones IV were synthesized by a known method – the coupling of 2-aminoanthracene with diazonium salts, the cyclization of the 1-arylazo-2-aminoanthracenes (V) by the action of copper sulfate [8], and subsequent oxidation of the 2-arylanthra[1,2-d]triazoles (VI) by chromic acid [7]. We obtained some of the anthraquinonetriazoles (IV) via a different route – by azo coupling of sulfate esters of 2-aminoanthrahydroquinones (VII) [9], subsequent conversion of the products to 1-arylamino-2-aminoanthraquinones (VIII), and final treatment with chromic anhydride. This method is convenient for the synthesis of 2-chloroanthraquinonetriazoles, since the sulfate ester of 3-chloro-2-aminoanthrahydroquinone is the intermediate used in industry. (See scheme an following page.)

We found that anthraquinonetriazoles IV, like anthraquinonediazoles I-III, undergo direct amination. Quinones IV are directly converted to 4-amino derivatives IX on heating with sufficiently basic primary and secondary aliphatic or heterocyclic amines. The introduction of sodium amide, which increases the nucleophilicity of the reagent owing to the formation of sodium arylamide, is necessary when the reaction is carried out with aromatic amines.

The identical character of the substances obtained from 2-phenylanthraquinonetriazole (IVa) and from its 4-chloro derivative on reaction with cyclohexylamine (IXa) or with morpholine (IXb) constitutes evidence for the direction of the amination. The location of the amino group in the anthraquinone ring in the β posi-

*See [1] for communication XXVI.

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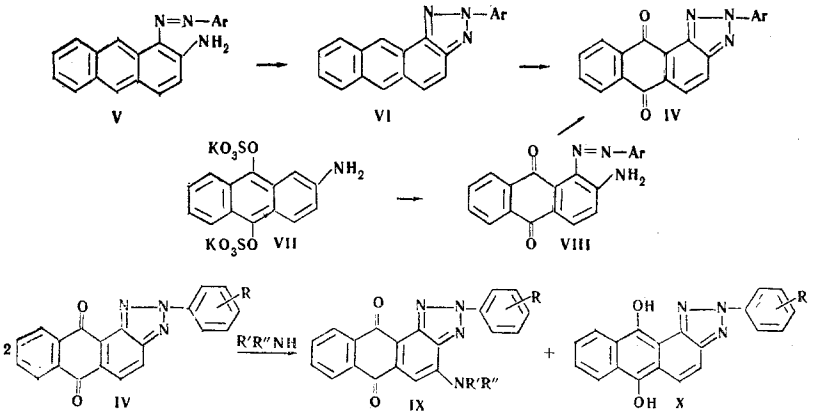


tion is also confirmed by the absence in the IR spectrum of the cyclohexylamino derivative (IXa), which contains a secondary amino group, of the splitting of the band of the carbonyl vibrations (ν_{CO} 1670 cm^{-1}) that is characteristic for α-alkyl- and α-arylaminoanthraquinones [10].

The yields of the amino derivatives obtained by heating in the amine in an inert atmosphere (argon) are ~50% but increase to 90-92% when air is passed through the reaction mixtures. The initially formed product of the addition of the amine to the anthraquinonetriazole is apparently oxidized by the starting quinone, which is reduced to the correspeonding hydroquinone (X) and subsequently regenerated by air oxidation. 2-Phenyl-6,11-dihydroxyanthratriazole (X, R=H), which is obtained by the reduction of IVa with stannous chloride, is, in fact, oxidized rapidly to the quinone in amines and alkaline solutions. The difference from anthraquinonediazoles I-III, in which amination proceeds in high yields without the participation of air oxygen with profound destruction of a portion of the starting quinone [2-4], is due to the high resistance of the 1,2,3-triazole ring to the action of reducing agents as compared with the rings of 1,2,5-X-diazoles (X = O, S, and Se).

The kinetics of the nucleophilic substitution of halogen in the corresponding 4-chloro derivatives (XI) were studied for a quantitative comparison of the activating effect of a heteroring in 2-arylanthraquinonetriazoles IV and anthraquinonediazoles I-III.

It is known that a halogen in the β position of anthraquinone is usually only slightly labile. At the same time, replacement of a halogen atom by an amine residue in heterocyclic quinones XI is readily accomplished in solutions, even at 20°C. The 4-chloro-substituted XI are arranged in the order $O \gg S > Se > NC_6H_5$ with respect to the magnitude of the rate constant as a function of the central heteroatom X (Table 1).

The reactivities in a group of anthraquinone-1,2,5-X-diazoles increase symbatically with increasing electronegativity of the X heteroatom, but the activity of 2-phenylanthraquinonetriazole is less than might be expected from the high electronegativity of nitrogen as compared with sulfur or selenium [11].

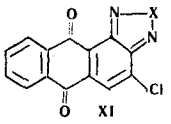
One of the reasons for the lower activity of 2-arylanthraquinonetriazoles IV is the electron-donor effect of the phenyl group in the 2 position. The character of this effect follows from an examination of the electronic spectra of 2-phenylanthraquinonetriazoles IV that contain substituents in the ortho and para positions of the phenyl ring.

The presence of an electron-donor substituent in the para position of the phenyl ring causes a bathochromic shift of the long-wave band, the magnitude of which (see Table 3) correlates with the electrophilic σ_n^+ constants in accordance with the equation

$$\nu_{max} = 26570 + 2816 \cdot \sigma_n^+ \text{ cm}^{-1} \quad (n=5,\ r=0.995,\ s=111 \text{ cm}^{-1}).$$

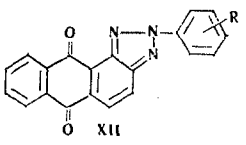
This sort of picture corresponds to the behavior of p,p'-disubstituted benzenes that contain a fixed electron-acceptor substituent [12], the role of which in this case is played by the anthraquinonetriazole ring. Substituents in the ortho position of the phenyl ring have a different effect, in that, regardless of their character, they shift the absorption band to the short-wave region. Thus a methoxy group, which leads to a bathochromic shift of ~30 nm in the para position, shifts the maximum by ~30 nm to the opposite side in the ortho position. An acceptor substituent (a nitro group, for example) causes a considerably larger short-wave shift in the ortho position than in the para position (see Fig. 1). A similar ortho-substituent effect is caused by steric hindrance to coplanar orientation, as a result of which, the phenyl group is turned about the C–N bond, and its donor effect is reduced.

TABLE 1. Rate Constants for the Pseudo-Monomolecular Reaction of 4-Chloro-Substituted Quinones (XI) with Morpholine in Dimethylformamide at 20° C



X	$\kappa \cdot 10^2$, sec^{-1}	Relative rate
O	~180	>150
S	8,60	8,2
Se	5,10	4,8
NC_6H_5	1,05	1,0

TABLE 2. Rate Constants of the Pseudo-Monomolecular Reaction of 4-Chloroanthraquinonetriazoles XII with Piperidine in Dioxane at 20° C



R	$\kappa \cdot 10^3$, sec^{-1}	Relative rate
H	4,50	1,0
p-OCH_3	2,61	0,58
p-CH_3	3,10	0,70
p-NO_2	12,60	2,8
o-NO_2	22,70	5,0

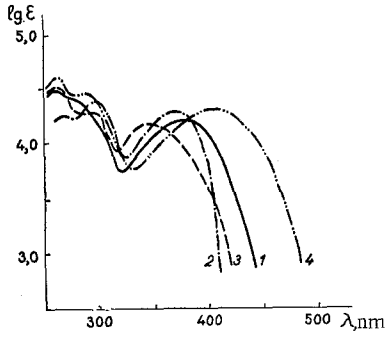


Fig. 1. Absorption spectra (in chloroform): 1) 2-phenylanthra[1,2-d]triazole-6,11-dione (IVa); 2) 2-(4-methoxyphenyl)anthra[1,2-d]triazole-6,11-dione (IVg); 3) 2-(4-nitrophenyl)anthra[1,2-d]triazole-6,11-dione (IVb); 4) 2-(2-nitrophenyl)anthra[1,2-d]-triazole-6,11-dione (IVc).

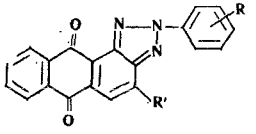
As the donor effect of the phenyl group weakens, the rate of nucleophilic substitution of the chlorine in the 4 position of the phenylanthraquinonetriazole increases. Owing to the superimposition of the steric effect, the introduction of a nitro group into the ortho position accelerates the reaction to a greater degree than in the para position; however, the introduction of a donor substituent into the para position reduced the reaction rate (Table 2).

When an amino group is incorporated into the 4 position of the ring of 2-phenylanthraquinonetriazoles, a new band corresponding to intramolecular transfer of electron density from the amine nitrogen to the ring ($2p_z\pi^*$ transition) in anthraquinone derivatives [13, 14] appears in the visible region. The effect of substituents in the phenyl ring of 4-amino derivatives IX is less than in the starting anthraquinonetriazoles and opposite in sign: donor substituents induce short-wave shifts, while acceptor substituents induce long-wave shifts. In this case, the 2-phenylanthraquinonetriazole ring as a whole, including the phenyl group, acts as an electron acceptor.

The nucleophilic substitution of halogen is far from being a complete model for the more complex nucleophilic addition, which leads to replacement of a hydrogen atom. The differences in the reactivities, which are due to the nature of heteroatom X, are considerably greater for unsubstituted quinones I-IV than for 4-chloro derivatives XI. 2-Arylanthraquinonetriazoles IV require much more severe conditions for their amination and do not undergo most of the other reactions with nucleophilic agents that are characteristic for anthraquinonediazoles I-III. The presence of an aryl group in the 2 position is apparently not the only and probably not the chief reason for the lower activity of 2-arylanthraquinonetriazoles IV as compared with anthraquinonediazoles I-III.

The increased reactivity of the 4-position of quinones I-IV for nucleophilic attack depends not only on the electrophilicity of the grouping that exerts an electron-acceptor effect but also on the effectivness of the transmission of this effect to the reaction center. The increased electronic conductivity of anthraquinonediazoles I-III is due to the presence, in the ring adjacent to the heteroring, of a partially localized dienic system [15], the existence of which is attested to by measurements of the bond lengths in anthraquinoneoxadiazole I and also by measurements of the bond lengths [16] in benzothiadiazole XIII and benzoselenadiazole XIV. The interatomic distances in benzotriazoles were not determined, but the distribution of the bonds in them can be judged on the basis of an analysis of the PMR spectra [17].

TABLE 3. 2-Arylanthra[1,2-d]triazole-6,11-diones

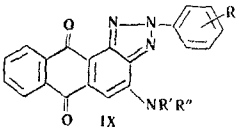


Compound	R	R′	mp, °C	λ_{max}, nm (log ε) (in chloroform)	Empirical formula	Found, %				Calc., %			
						C	H	Cl	N	C	H	Cl	N
IVa	H	H	278—279	380 (4,08)	$C_{20}H_{11}N_3O_2$	73,87	3,21	—	12,65	73,84	3,41	—	12,91
IVb	*p*-NO_2*	H	343—344	370 (4,25)	$C_{20}H_{10}N_4O_4$	64,65	2,88	—	15,43	64,87	2,72	—	15,13
IVc	*o*-NO_2	H	290—292	346 (4,19)	$C_{20}H_{10}N_4O_4$	64,95	2,99	—	15,41	64,87	2,72	—	15,13
IVd	*p*-Cl	H	222—223	378 (4,23)	$C_{20}H_{10}ClN_3O_2$	66,97	2,90	9,76	11,69	66,77	2,80	9,85	11,68
IVe	*o*-Cl	H	278—279	347 (4,01)	$C_{20}H_{10}ClN_3O_2$	66,52	2,96	9,64	11,59	66,77	2,80	9,85	11,68
IVf	*p*-CH_3	H	299—300	388 (4,24)	$C_{21}H_{11}N_3O_2$	74,12	3,91	—	12,45	74,33	3,86	—	12,38
IVg	*p*-OCH_3	H	262—263	410 (4,27)	$C_{21}H_{13}N_3O_3$	71,16	3,57	—	12,00	70,98	3,69	—	11,83
IVh	*o*-OCH_3	H	266—267	350 (3,84)	$C_{21}H_{13}N_3O_3$	71,05	3,83	—	11,69	70,98	3,69	—	11,83
IVi	*p*-NH_2†	H	342—343	440 (4,04)	$C_{20}H_{12}N_4O_2$	70,38	3,46	—	16,40	70,58	3,55	—	16,46
IVj	*p*-$NHCOCH_3$	H	319—320	400 (4,20)	$C_{22}H_{14}N_4O_3$	69,34	3,63	—	14,86	69,10	3,69	—	14,70
XIIa	H	Cl	324—325	370 (4,15)	$C_{20}H_{10}ClN_3O_2$	66,51	2,94	10,12	11,78	66,77	2,80	9,85	11,68
XIIb	*p*-OCH_3	Cl	257—258	400 (4,16)	$C_{21}H_{12}ClN_3O_3$	64,58	3,23	8,82	10,54	64,71	3,10	9,09	10,77
XIIc	*o*-OCH_3	Cl	238—239	375 (3,87)	$C_{21}H_{12}ClN_3O_3$	64,76	3,22	9,06	10,49	64,71	3,10	9,09	10,77
XIId	*p*-NO_2	Cl	318—319	360 (4,33)	$C_{20}H_9ClN_4O_4$	59,35	2,48	8,95	13,63	59,35	2,24	8,76	13,84
XIIe	*o*-NO_2	Cl	301—303	343 (4,12)	$C_{20}H_9ClN_4O_4$	59,37	2,39	8,98	14,16	59,35	2,24	8,76	13,84
XIIf	*p*-Cl	Cl	289—291	377 (4,20)	$C_{20}H_9Cl_2N_3O_2$	61,03	2,10	17,86	10,70	60,94	2,30	17,99	10,66
XIIg	*p*-CH_3	Cl	284—285	385 (4,15)	$C_{21}H_{12}ClN_3O_2$	67,63	3,18	9,26	11,23	67,47	3,24	9,48	11,29

*mp 325° C [7].

†mp 356° C [7].

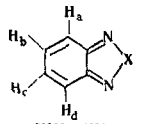
TABLE 4. 4-Amino Derivatives of 2-Arylanthra[1,2-d]triazole-6, 11-diones (IX)



IX

Designation	R	R'R"NH	mp. °C	λmax, nm (in chloroform)	Empirical formula	Found, %			Calc., %			Yield,%*
						C	H	N	C	H	N	
a	H	Cyclohexylamine	244—245	510 (3,91)	$C_{26}H_{22}N_4O_2$	74,11	5,38	13,40	73,91	5,25	13,26	85
b	H	Morpholine	284—285	506 (3,98)	$C_{24}H_{18}N_4O_3$	70,17	4,67	13,64	70,23	4,42	13,65	87
c	H	Aniline	205—206	502 (3,87)	$C_{26}H_{16}N_4O_2$	74,53	3,99	13,20	74,99	3,87	13,46	70
d	H	Piperidine	252—253	532 (3,95)	$C_{25}H_{20}N_4O_2$	73,47	5,01	13,58	73,51	4,94	13,72	92
e	p-NO_2	Piperidine	289—290	542 (3,98)	$C_{25}H_{19}N_5O_4$	66,42	4,28	15,38	66,22	4,22	15,44	76
f	o-NO_2	Piperidine	270—271	538 (4,15)	$C_{25}H_{19}N_5O_4$	66,20	4,48	15,71	66,22	4,22	15,44	88
g	p-Cl	Piperidine	266—267	530 (4,15)	$C_{25}H_{19}ClN_4O_2$	67,91	4,42	12,93	67,80	4,32	12,65	91
h	o-Cl	Piperidine	220—221	528 (4,07)	$C_{25}H_{19}ClN_4O_2$	68,06	4,26	12,61	67,80	4,32	12,65	90
i	p-NH_2	Piperidine	297—298	522 (4,03)	$C_{25}H_{21}N_5O_2$	71,00	5,12	16,48	70,90	5,00	16,53	50
j	p-CH_3	Piperidine	270—271	534 (4,06)	$C_{26}H_{22}N_4O_2$	74,07	5,45	13,28	73,92	5,25	13,26	74
k	p-CH_3O	Piperidine	246—247	532 (4,05)	$C_{26}H_{22}N_4O_3$	71,44	5,10	12,78	71,22	5,06	12,78	81
l	o-CH_3O	Piperidine	231—232	534 (3,98)	$C_{26}H_{22}N_4O_3$	71,52	5,16	12,53	71,22	5,06	12,78	80

*After chromatographic purification.



XIII X = S,
XIV X = Se,
XV X = NCH3

XIII – XV

The ratios of the spin–spin coupling constants of the protons of the benzoid ring in systems with equalized bonds are as follows: $J_{bc}/J_{ab} \cong 1$, and $J_{ac}/J_{ad} > 1$. In systems with localized single and double bonds, $J_{bc}/J_{ab} \cong 0.5$, and $J_{ac}/J_{ad} < 1$. 2-Methylbenzotriazole XV occupies an intermediate position [17]: $J_{bc}/J_{ab} = 0.72$, and $J_{ac}/J_{ad} \cong 1$, and the disruption of the uniformity of the bonds in it is less than in benzothiadiazole XIII ($J_{bc}/J_{ab} = 0.54$) [18] or in benzoselenadiazole XIV ($J_{bc}/J_{ab} = 0.63$) [19].

The lower degree of alternation of the bonds, which is caused by the lower electronic conductivity of the ring adjacent to the heteroring, also leads to a decrease in the activity of 2-arylanthraquinonetriazoles IV as compared with anthraquinonediazoles I-III in nucleophilic addition reactions.

EXPERIMENTAL

2-Arylanthra[1,2-d]triazole-6,11-diones (IV). (Table 3). A) A solution of a diazonium compound, prepared by diazotization of 0.03 mole of the appropriate amine in 20 ml of 15% hydrochloric acid, was added at 10°C to a solution of 5.85 g of 2-aminoanthracene [20] in 300 ml of dioxane, and the mixture was stirred for 30 min. The azo compound was isolated by the addition of 300 ml of 10% sodium acetate solution to give 85-98% yields of products. A solution of 0.02 mole of the azo compound in 60 ml of pyridine was added to a suspension of 15 g of copper sulfate in 60 ml of 50% aqueous pyridine, and the mixture was refluxed for 2 h and diluted with 120 ml of water. The resulting precipitate was removed by filtration to give pale-yellow needles (from chlorobenzene) of the anthratriazole, which has pronounced blue fluorescence in UV light. A total of 3 g of 70% chromic anhydride was added in portions with heating to a suspension of 0.06 mole of the anthratriazole in 60 ml of acetic acid, and the mixture was refluxed for 30 min and cooled. The precipitate was separated to give 80-90% of light-yellow needles (from acetic acid) of quinone IV.

4-Chloro-2-phenanthraquinonetriazole XIIa was similarly obtained from 3-chloro-2-aminoanthracene. To obtain 2-(4-aminophenyl)anthraquinonetriazole IVi, 6 g of stannous chloride was added to a suspension

of 0.002 mole of nitro compound IV in 100 ml of hydrochloric acid, and the mixture was refluxed for 20 min and filtered hot. The yellow crystals of the hydrochloride were separated and treated with 5% ammonium hydroxide while air was bubbled through the system. The reduction of nitro compound IV with stannous chloride in glacial acetic acid gave yellow needles (from acetic acid) of 6,11-diacetoxy-2-(4-acetamidophenyl)anthra[1,2-d]triazole with mp 329-330°C. Found: C 66.47; H 4.47; N 12.04%. $C_{26}H_{20}N_4O_5$. Calculated: C 66.66; H 4.30; N 11.96%. This compound was then converted to quinone IVi by alkaline hydrolysis and oxidation.

4-Acetamido derivative IVj was obtained as orange needles (from acetic acid) by the acetylation of amino compound IVi with acetic anhydride.

B) A solution of 0.05 mole of the appropriate 1-arylazo-2-aminoanthraquinone in 30 ml of acetic acid was refluxed for 30 min with 3 g of chromic anhydride and cooled. The resulting precipitate of the anthraquinonetriazole was recrystallized from acetic acid to give 60-70% of product. This method was used to obtain anthraquinonetriazoles IVa and XIIa-g.

1-Arylazo-3-chloro-2-aminoanthraquinones. A solution of an arenediazonium salt, prepared by diazotization of 0.01 mole of amine in 15 ml of 10% hydrochloric acid, was added to a solution of 0.01 mole of the dipotassium salt of the disulfate ester of 3-chloro-2-aminoanthrahydroquinone and 2 g of potassium carbonate in 50 ml of pyridine. A total of 10 ml of 30% hydrogen peroxide and 200 ml of hydrochloric acid were poured into the mixture, and it was refluxed until the solution was decolorized. The resulting precipitate was removed by filtration, washed with water, and chromatographed in chloroform on aluminum oxide to give 50-70% of the azo compound.

1-Phenylazo-3-chloro-2-aminoanthraquinone. This compound had mp 214-215° C and λ_{max} 447 nm (log ε 4.24). Found: C 66.22; H 3.64; Cl 9.68; N 11.54%. $C_{20}H_{12}ClN_3O_2$. Calculated: C 66.40; H 3.40; Cl 9.81; N 11.61%.

1-(4-Nitrophenylazo)-3-chloro-2-aminoanthraquinone. This compound had mp 269-270°C and λ_{max} 465 nm (log ε 4.04). Found: C 58.93; H 2.94; Cl 8.82; N 14.01%. $C_{20}H_{11}ClN_4O_4$. Calculated: C 59.05; H 2.73; Cl 8.72; N 13.77%.

1-(4-Methoxyphenylazo)-3-chloro-2-aminoanthraquinone. This compound had mp 193-194° C and λ_{max} 460 nm (log ε 3.79). Found: C 64.25; H 3.48; Cl 9.07; N 10.68%. $C_{21}H_{14}ClN_3O_3$. Calculated: C 64.38; H 3.60; Cl 9.05; N 10.72%.

3-Chloro-2-aminoanthracene. A mixture of 20.6 g (0.08 mole) of 3-chloro-2-aminoanthraquinone, 480 ml of water, 55 ml of a 40% sodium hydroxide solution, and 55 g of zinc dust was stirred under reflux for 9 h, cooled, and filtered. The product was extracted from the solid by treatment with hot dimethylformamide to give 14.6 g (80%) of light-yellow leaflets (from dimethylformamide) with mp 235-235.5° C. Found: Cl 15.56; N 6.12%. $C_{14}H_{10}ClN$. Calculated: Cl 15.62; N 6.16%.

6,11-Dihydroxy-2-phenylanthra[1,2-d]triazole (X, R=H). This compound was obtained by refluxing 0.002 mole of quinone IVa in 70 ml of acetic acid with a solution of 5 g of stannous chloride in 10 ml of concentrated hydrochloric acid to give yellow needles (from acetic acid) with mp 272° C (dec.) that gave a red coloration in alkaline solutions. Found: C 73.15; H 3.75; N 12.80%. $C_{20}H_{13}N_3O_2$. Calculated: C 73.38; H 4.00; N 12.84%. The diacetate was obtained as pale-yellow needles (from acetic acid) with mp 293-294° C. Found: C 69.98; H 4.14; N 10.37%. $C_{24}H_{17}N_3O_4$. Calculated: C 70.06; H 4.17; N 10.12%.

4-Amino Derivatives of 2-Arylanthra[1,2-d]triazole-6,11-diones (IX) (Table 4). A mixture of 0.002 mole of anthraquinonetriazole IV and 15 g of amine was refluxed for 2 h while air was bubbled through the mixture. It was then poured into 5% hydrochloric acid, and the resulting precipitate was removed by filtration and chromatographed on aluminum oxide with elution by chloroform. The amino derivative obtained was recrystallized from chlorobenzene or dioxane. The reaction of 4-chloro-2-phenylanthraquinonetriazole XIIa with cyclohexylamine and morpholine under the same conditions gave substances that, according to their melting points and IR spectra, were identical to the compounds synthesized from 2-phenylanthraquinonetriazole IVa. In the reaction of quinone IVa with aniline, 0.005 mole of sodium amide was added, the mixture was heated, the quinone was added, and the mixture was refluxed for 2 h. In the experiment with piperidine, which was carried out under argon, the yield of IXd was 52%, and 43% of the starting quinone was regenerated.

Measurement of the Rate of the Reaction of 4-Chloro Derivatives XI and XII with Amines. An equal volume of a 1 M solution of morpholine or piperidine in dimethylformamide or dioxane was poured into a

10^{-3} M solution of the 4-chloro derivative in the same solvent, and the increase with time in the optical density at the wavelength corresponding to the absorption maximum of the corresponding amino compound was measured.

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